

Full Length Article

Facile synthesis of $W_2C@WS_2$ alloy nanoflowers and their hydrogen generation performanceThang Phan Nguyen^a, Soo Young Kim^b, Tae Hyung Lee^c, Ho Won Jang^c, Quyet Van Le^d, Il Tae Kim^{a,*}^a Department of Chemical and Biological Engineering, Gachon University, Seongnam-si, Gyeonggi-do 13120, Republic of Korea^b Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea^c Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Republic of Korea^d Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam

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ABSTRACT

Two-dimensional transition metal dichalcogenides such as MoS_2 and WS_2 nanosheets, nanoflowers, and nanoparticles have been investigated as potential materials for the hydrogen evolution reaction (HER). Besides 2D-TMDs, MXene materials, which are transition metal carbides/nitrides, are promising candidates for energy storage and conversion applications. In this work, alloys of tungsten carbides and tungsten disulfides have been fabricated through a facile hydrothermal method without using any complex structure of carbon or polymer source for carbonization. The fabricated alloys were characterized by X-ray diffraction analysis, field emission scanning microscopy, atomic force microscopy, Raman spectra, and X-ray photoelectron spectroscopy. The results indicated both W_2C and WS_2 have hexagonal structure in the alloy compound. $W_2C@WS_2$ nanomaterials exhibit abundant flower-shaped active sites ranging from 200 to 400 nm in size. The catalytic behavior of these alloys in the HER was studied through a three-electrode system. The results indicated that the catalytic performance was better than those of previous research and that the flower-shaped nanomaterials were superior to nanosheets, with a high double-layer capacitance of 12 mF cm^{-2} . This work, thus, introduced a simple approach to the synthesis of transition metal carbide/chalcogenide composites and demonstrated that these materials are promising in energy generation and storage applications.

1. Introduction

Currently, the growing demand for energy is a growing concern for society because of the limited fossil resources, such as charcoal and oil. In addition, burning of fossil energy causes severe environmental problems such as air pollution and global warming. Therefore, solutions producing environmentally friendly and renewable energy resources are very urgent. Among the various new energy resources, hydrogen produced from electro-splitting of water has become the most promising candidate because it is low cost, renewable, and scalable. Noble metals such as platinum and palladium are the commonly used catalysts for producing hydrogen, and show zero over potential over the hydrogen evolution reaction (HER) [1–3]. However, they are expensive and rare, which prevents their large-scale commercial production. Recently, two-dimensional transition metal dichalcogenides (2D-TMDs) such as MeS_2 ($Me = Mo$ or W) have attracted attention because of their superior properties. These materials have potential for high electrical

conductivity, thermal conductivity, charge carrier mobility, stability, and tunable band-gap, making them promising candidates for electronic and optoelectronic devices, such as transistors, solar cells, light-emitting diodes, and gas sensors [4–17]. Notably, they are considered as efficient catalysts for the HER and can potentially replace the expensive platinum catalysts [18]. Although 2D-TMDs without any treatment show the potential for catalytic activity, their performance is relatively low [19]. Many approaches for the improvement of the catalytic properties of 2D-TMDs have been studied. For example, the transformation of 2D-TMDs from the 2H phase to the 1T phase has significantly improved the HER performance [20–22]. The amorphous nature of materials were also investigated for large-scale hydrogen production [23,24]. Other morphologies of 2D-TMDs, such as nanoparticles, nanoflowers, and hierarchical TMDs, and their combination with graphene were also reported to exhibit significant improvements in the catalytic activities [25–29]. Nonetheless, the important parameter that hinders the performance of 2D-TMDs as catalysts in the HER

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is their low conductivity.

MXene materials are 2D transition metal carbide/nitrides with the formula M_n+1X_n , where M is a transition metal atom and X is a C or N atom [30]. MXene have been reported to exhibit good stability, electronic conductivity and electrochemical catalytic activity [31,32]. For example, Huang has successfully synthesized Mo_2C particles by preparing carbon flowers using the calcination method and showed that they possess high performance and a low Tafel slope of 55 mV dec^{-1} [33]. Gong et al. fabricated W_2C particles on multiwalled carbon nanotubes via carburization at 900°C in a furnace, which can play dual roles as electrochemical catalysts and photoelectron catalysts for the HER [34]. More recently, Cheng et al. synthesized MoS_2 /guar gum carbon nanoflowers which resulted in a combination of a MoS_2 structure and a molybdenum carbide structure, showing superior electrocatalytic properties with a Tafel slope of 34 mV dec^{-1} [35]. Thus, it is expected that a combination of tungsten sulfides and carbides could improve the electronic and catalytic properties of materials. In this study, a facile hydrothermal method was employed for the preparation of nanoflower tungsten carbide and tungsten disulfide alloys ($W_2C@WS_2$) for using in the HER. The structures and properties of these materials, such as morphology and chemical composition, were fully characterized by XRD, FE-SEM, AFM, Raman spectra, and XPS measurements. The electrochemical measurements showed that the performance of WS_2/W_2C alloys in the HER is significantly improved in comparison to that of bare nanosheets and as prepared WS_2 nanoflowers. We believe that these WS_2/W_2C alloys are promising candidates not only for the HER but also for other energy-storage devices such as supercapacitors and batteries.

2. Experimental details

2.1. Chemical materials

Tungsten (VI) chloride (WCl_6 , 99.9% trace metals basis) and thioacetamide (C_2H_5NS , 99%) were purchased from Sigma Aldrich. Absolute ethanol was provided by Alpha Aesar. Deionized (DI) water ($18.3\text{ M}\Omega\text{ cm}^{-1}$) was obtained from Millipore Milli-Q.

2.2. Co-synthesis of $W_2C@WS_2$ nanoflowers

Tungsten (VI) chloride, a moisture-sensitive chemical, was chosen as the W source. To avoid any unexpected reaction, WCl_6 powder was retrieved from an Ar/N_2 -filled glovebox. The WCl_6 powder was kept in a 20 mL tube with a cap, and the experiment was carried out inside of a fume hood. The $W_2C@WS_2$ material was synthesized by the hydrothermal method. 0.6 g of WCl_6 was mixed with 4 mL absolute ethanol under stirring. Thioacetamide was prepared by mixing 1.2 g of the powder with 4 mL absolute ethanol by stirring at a warm temperature (40°C). A higher temperature can cause hydrolysis of thioacetamide. Then, the WCl_6 solution was quickly mixed with the thioacetamide solution while stirring. The color of the mixture immediately changed from dark yellow to black. Twenty milliliters of DI water were added to the solution, and the mixture was stirred for 10 min. The solution was transferred to a 100 mL Teflon line autoclave and heated in an oven at 250°C for 20 h. A black precipitation formed at the bottom of the Teflon line, was collected, and washed several times with ethanol and DI water. $W_2C@WS_2$ was obtained as a powder after drying at 60°C . Finally, the material was dispersed in DI water with sonication and then coated for characterization experiments.

2.3. Electrochemical measurements

The working electrode was prepared by mixing 1 mg of $W_2C@WS_2$ in 1 mL of DI water and 80 μL of Nafion (5%) as the stabilizer, then drop-coating the mixture on a glassy carbon electrode, and drying the electrode at 30°C . The diameter of the glassy carbon electrode (working

electrode) was 3 mm. The hydrogen evolution reaction was monitored by a three-electrode system, with an electrolyte of 0.5 M H_2SO_4 . A carbon electrode was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. A linear sweeping was performed at a scan rate of 10 mV s^{-1} . A rapid scan of 50 mV s^{-1} was selected for the cyclic voltammetry measurement. Double-layer capacitance (C_{dl}), electrochemical surface area (ECSA), and turn-over potential (TOF) were measured at the scanning rates of 10, 20, 30, 40, and 50 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was carried out at a potential of 230 mV versus a reversible hydrogen electrode at frequency ranging from 100 kHz to 0.1 Hz. All the electrochemical measurements were carried out on an Ivium potentiostat V55630.

2.4. Materials characterization

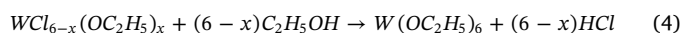
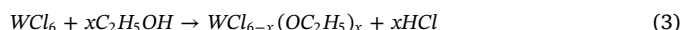
XRD (D8 ADVANCE, by Bruker AXS), FE-SEM (SIGMA, by Carl Zeiss), non-contact-mode AFM (XE-100, by PSIA), Raman spectroscopy (Lab RAM HR, by Horiba JobinYvon) and transmission electron microscopy (TEM, JEM-2100F, by JEOL) were used to study the structure and size of materials. XPS (Axis Ultra DLD, by Kratos) operated at a base pressure of 1.6×10^{-10} mbar at 300 K with a monochromatic Al K α line was also performed to study the chemical composition and the bonding level of materials.

3. Results and discussion

Many studies have reported hydrothermal reduction of WCl_6 and thioacetamide in a normal process without ethanol, resulting in the formation of WS_2 [25,36]. The reaction processes are outlined in Eqs. (1) and (2): [37]

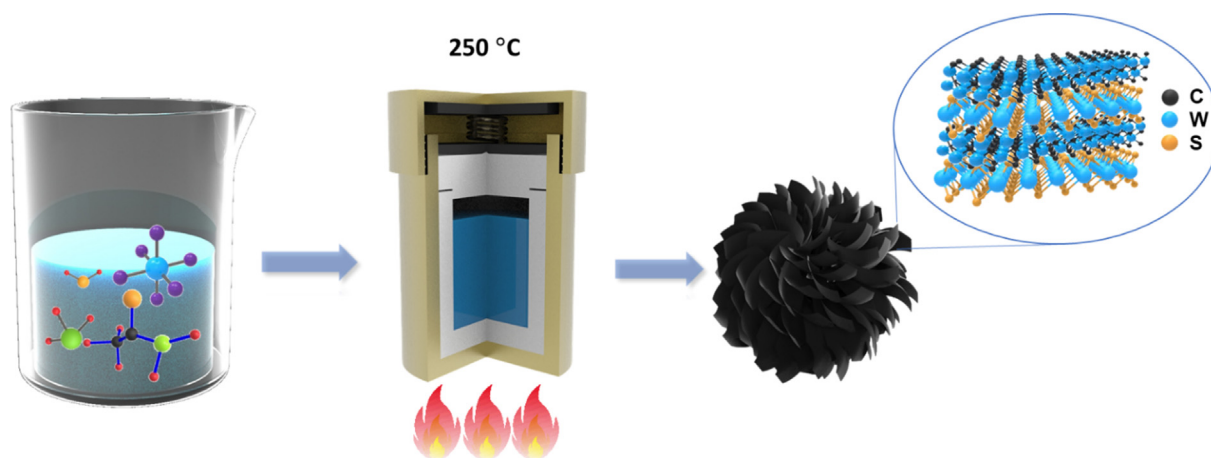
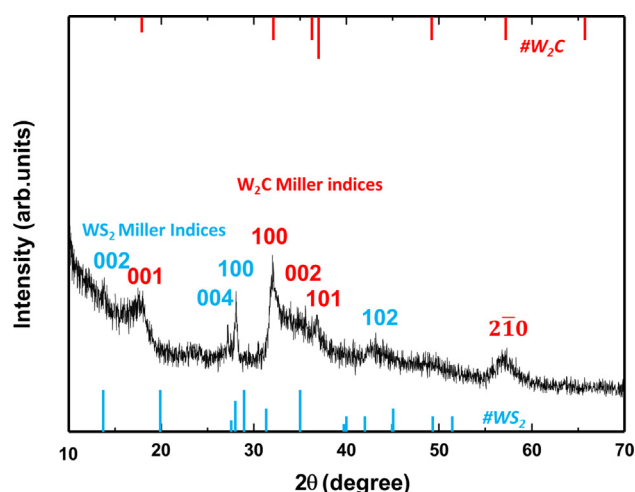


Ethanol is a well-known solvent for WCl_6 for preparing WO_3 , as shown in the reactions (3) and (4): [38,39]



After the reaction (3), the WCl_6 solution in ethanol turned yellow; it further turned blue when kept in air. If the ethanol continuously reacts with $WCl_{6-x}(OC_2H_5)_x$, the solution becomes transparent. In this study, we added thioacetamide when the solution was yellow to form the pre-hydrothermal treated solution. This process may prevent the reaction of ethanol with tungsten chloride. The appearance of H_2S and NH_3 from the hydrolysis of thioacetamide in Eq. (1), which are reducing agents, may have a specific role in carburization process. The synthesis of composite nanoflower materials were described in Scheme 1.

The crystal structure of the $W_2C@WS_2$ materials has been confirmed by the XRD patterns shown in Fig. 1. Analysis of the peaks using Miller indices shows that both WS_2 [40,41] and WC [42,43] have a hexagonal structure. The co-existence of W_2C and WS_2 XRD peaks indicated the co-formation of these materials with a similar hexagonal lattice structure. Both W_2C and WS_2 have many XRD peaks, which suggested the complex growth of these materials. When looking into the Fig. 1, sharp peaks at $25\text{--}28^\circ$ could be observed, which indicates major growing orientation directions (1 0 0) and/or (0 0 4) of the WS_2 phase. Other weak peaks illustrate the minor growing orientation. The formation of W_2C could be explained by the reduction of the carbon atom from thioacetamide or ethanol, which then combined with the W ion during the hydrothermal process. We compared the results with those of the method without ethanol and found that WS_2 always formed without a W_2C structure. This is similar to the WS_2 hydrothermal processes reported in recent studies [36,44]. It is easier to obtain the carbide of W_2C using our method when compared with previous studies, which needed

Scheme 1. Synthetic process of $W_2C@WS_2$ nanoflowers.Fig. 1. XRD pattern of nanoflower showing hexagonal structures of WS_2 and W_2C using Miller indices.

a rich carbon source such as a polymer using the calcination process or a polymer using the hydrothermal process [34,35,45]. The successful synthesis of tungsten carbide/sulfide alloy is promising to have further studies with other transition metal such as Mo, Ti, V, etc. in composition carbides and sulfides.

The morphologies of the material revealed by the FE-SEM and AFM measurements are shown in Fig. 2. Nanoflowers of $W_2C@WS_2$ which are made of many flower-shaped nanosheets are shown in Fig. 2(a). The sizes of nanoflowers were measured to be approximately 200–500 nm. To further gain insights into their layer structure, the $W_2C@WS_2$ powder was sonicated in DI water and then spin-coated on a silicon substrate for FE-SEM and AFM measurements. The nanosheets exhibited a uniform surface as shown in Fig. 2(b), which indicated that the size, shape, and the thin layer nature of nanosheets are different from those of nanoflowers. The characterization of thickness and the lateral size confirmed that the material is formed of thin layers of thickness less than 10 nm and lateral sizes in the range of 50–150 nm (Fig. 2(c) and 2(d), respectively). This is an interesting structure formed by the hydrothermal method by combining two materials into a uniform shape. It indicates the compositions of W_2C and WS_2 ($W_2C@WS_2$) were well formed during the thermal treatment. This can be an easy method for large synthesis of W_2C/WS_2 nanosheets with high uniform thin layer.

TEM was used to characterize the material structure, as shown in Fig. 3(a–f). The flower shape of the materials is sharp with many leaves, which are the nanosheets of these layered materials. Fig. 3(a) and (d)

show a few layers and the multilayer structure of the nanosheets, of different interlayer spacings of 1.2 nm to 0.86 nm and the distance spacing of the (0 0 4) plane in WS_2 of 0.32 nm. The HRTEM image in Fig. 3(b) and (c) revealed the co-existence of W_2C (1 0 1) and WS_2 (1 0 0) with lattice distances of 0.23 and 0.27 nm, respectively. By sonication to separate W_2C and WS_2 , the selected-area electron diffraction (SAED) patterns were well recorded in Fig. 3(e) and (f) which confirmed again the hexagonal structure of WS_2 and W_2C .

Another confirmation of the structure and chemical bonding of these transition metal chalcogenides and carbide material is by the Raman spectra, shown in Fig. 4. For this experiment, the materials were coated on a SiO_2 substrate and excited by a laser source at an excitation wavelength of 532 nm. Transition metal dichalcogenides such as WS_2 materials have an in-plane vibration mode (E_{2g}^1) and an out-of-plane vibration mode (A_{1g}) located in the range 300–500 cm^{-1} . Inset figure shows two vibration mode located at 351 cm^{-1} (E_{1g}^1) and 415 cm^{-1} (A_{1g}). These results agreed with the Raman peaks of the WS_2 nanomaterial reported previously [40,46]. The vibration modes of W_2C were also confirmed in the range of 600–900 cm^{-1} . These results are also similar to other reports about W_2C [47,48]. The appearance of carbide also showed the D and G bands of the Raman spectrum of the nanoflower materials. The formation of $W_2C@WS_2$ is highly similar to the formation of $MoS_2@MoC$ reported by Chen et al. [35]. They used the hydrothermal reduction method with ammonium molybdate tetrahydrate and thiourea with guar gum as the carbon source for the carbide formation. However, the crystallization of molybdenum carbides was not clearly recorded. In our method, with a simple process using WCl_6 and thioacetamide only, tungsten carbides can be formed together with WS_2 . We believe that this material will improve the catalytic and electronic properties of chalcogenide materials (WS_2) and MXene materials (W_2C).

Fig. 5 shows the XPS spectra of $W_2C@WS_2$ nanoflowers to study the chemical composition of the material surface. To understand the complex peaks of the carbon atom on the surface of materials, the carbon peaks were deconvoluted into three peaks as shown in Fig. 5(a), which shows the peaks of $C=C/C-C$, $C-O$, and $C-OH$ bonding at 284.7, 286.3, and 288.5 eV, respectively. In addition, strong $W 4f_{7/2}$ and $W 4f_{5/2}$ peaks are observed between 30 and 35 eV, which indicates the high purity of materials. After deconvolution, the spectrum indicated the $W-C$ bonding contributes to the peaks of $4f_{7/2}$ and $W 4f_{5/2}$ at 31.9 and 34.1 eV, respectively, while $W-S$ bonding contributes to the peaks of $4f_{7/2}$ and $W 4f_{5/2}$ at 32.4 and 34.6 eV, respectively. It is noted that the strong peak of $W-C$ bonding and weak peak of $W-S$ bonding illustrate the small amount of WS_2 in the composite. This is in good agreement with XRD results. Finally, small oxidation peaks resulting from $W-O$ bonding were observed, which appeared at about 35.6 eV for $W 4f_{7/2}$ and 37.8 eV for $W 4f_{5/2}$. Sulfur atoms also showed a doublet

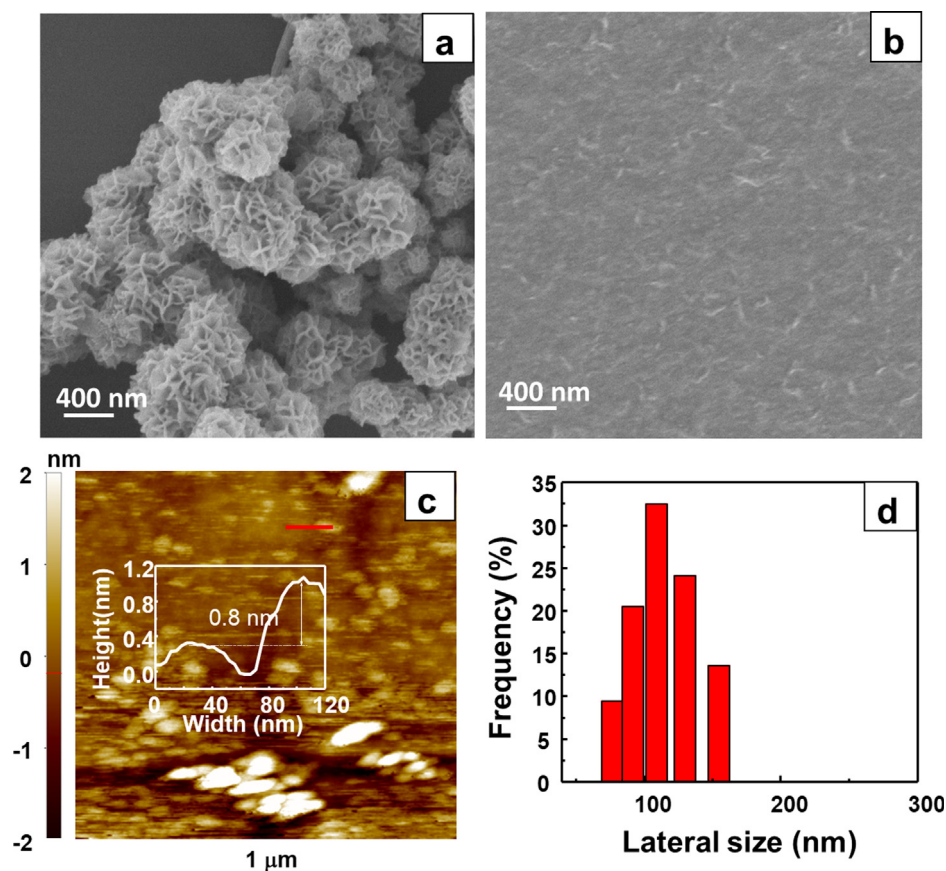


Fig. 2. FE-SEM images of $W_2C@WS_2$ nanoflowers (a) and nanosheets after sonication (b). AFM images of nanosheets (c) and the lateral size statistic (d) of $W_2C@WS_2$ nanosheets.

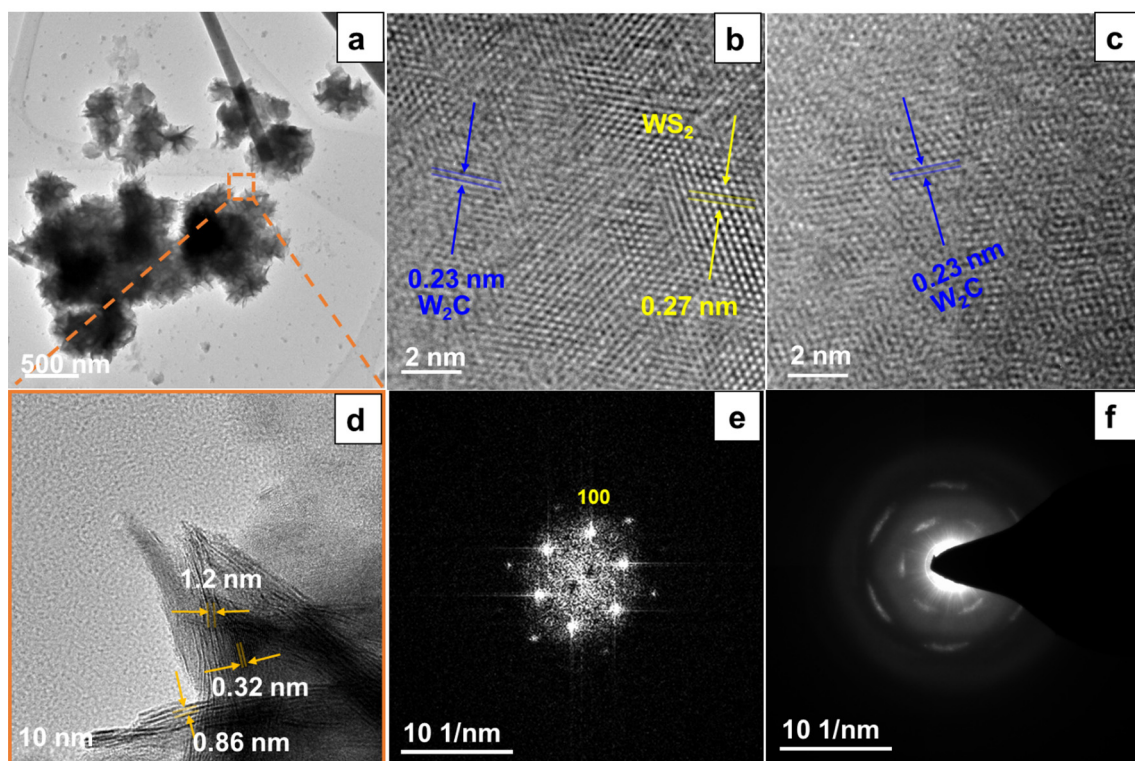


Fig. 3. (a, d) TEM images of the $W_2C@WS_2$ nanoflower and leafy structure with a few-layer and multilayer structures; HRTEM image and SAED pattern of (b, e) $W_2C@WS_2$ nanoflowers and (c, f) a W_2C nanosheets.

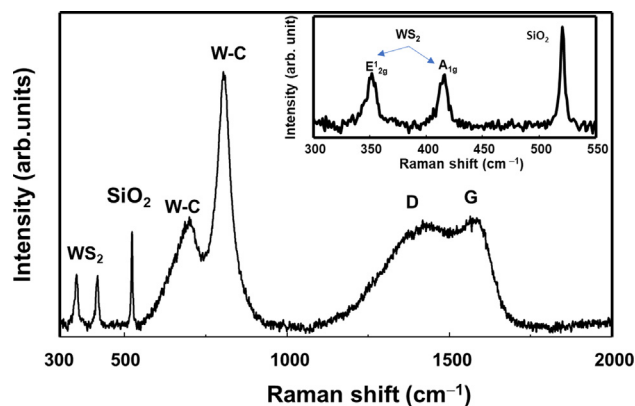


Fig. 4. Raman spectrum of WS₂, W₂C, D, G bands of carbon under a laser excitation of 532 nm with the inset of detailed WS₂ Raman spectrum.

of S 2p_{3/2} and S 2p_{1/2} peaks at 162.1 and 163.3 eV, respectively. There was a small peak of S–O bonding, which indicates that the sulfur was slightly oxidized on the surface. By using the atomic sensitivity factor, the concentrations of W, S, C, and O were calculated to be 39.36, 26.31, 26.09, and 8.24%, respectively. Notably, WS₂/W₂C and the oxygen incorporated WS₂ have been reported for the improvement of hydrogen evolution reaction performance [47,49]. Y. Li and his colleagues suggested the existence of W–C and W–S led to the improved catalytic

performance in comparison with the bare W₂C/nano porous carbon [47]. The oxygen incorporated WS₂ consisted of W–S and W–O bindings, and its HER property was much higher than pure WS₂ material in both 1T and 2H phase [49]. Therefore, the co-existence of W–C, W–S, and W–O is believed to exhibit synergistic effects on the enhancement of catalyst properties.

The catalytic activity of W₂C@WS₂ nanoflowers was investigated in an acidic medium of 0.5 M H₂SO₄ using a three-electrode system. Fig. 6(a) shows the polarization curves of the W₂C@WS₂ nanoflower in comparison with nanosheets of the material obtained through sonication and as prepared WS₂ nanoflowers. The onset of both materials is quite similar at ~170 mV for the nanoflower and ~180 mV for the nanosheets. WS₂ nanoflowers shows a better onset potential at ~150 mV. To evaluate the performance of nanoflowers in the HER, the Tafel slopes were plotted as shown in Fig. 6(b), which shows the slope of nanoflower materials (55.4 mV dec⁻¹) to be much better than nanosheets (80 mV dec⁻¹) and WS₂ nanoflower (85 mV dec⁻¹). The impedance of W₂C@WS₂ nanosheets and nanoflowers were similar (~200 Ω); however, they are smaller than that of WS₂ nanoflower (~400 Ω), as shown in the electrochemical impedance spectra of Fig. 6(c). This implies that the existence of W₂C help materials have better conductivity. The double-layer capacitance (C_{dl}) of these materials was calculated via scanning at the scan rates of 10, 20, 30, 40, and 50 mV s⁻¹. Fig. 6(d) shows that the capacitance of the electrode in nanoflowers (12.28 mF cm⁻²) is almost twice that of nanosheets (6.3 mF cm⁻²), which is much better than that of as prepared WS₂

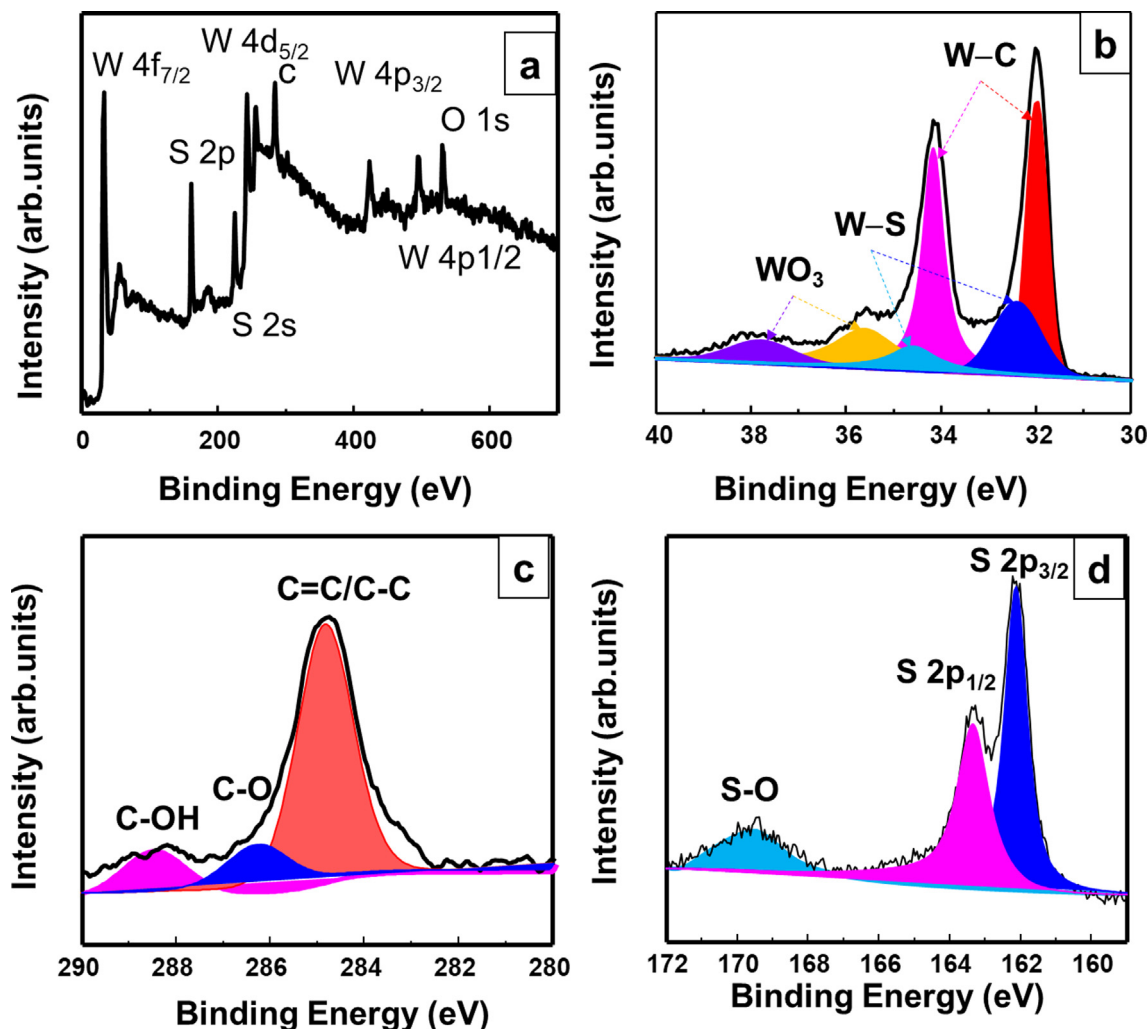


Fig. 5. XPS spectra of (a) survey scan of surface, (b) W 4f, (c) C 1s, and (d) S 2p of W₂C@WS₂ nanoflowers.

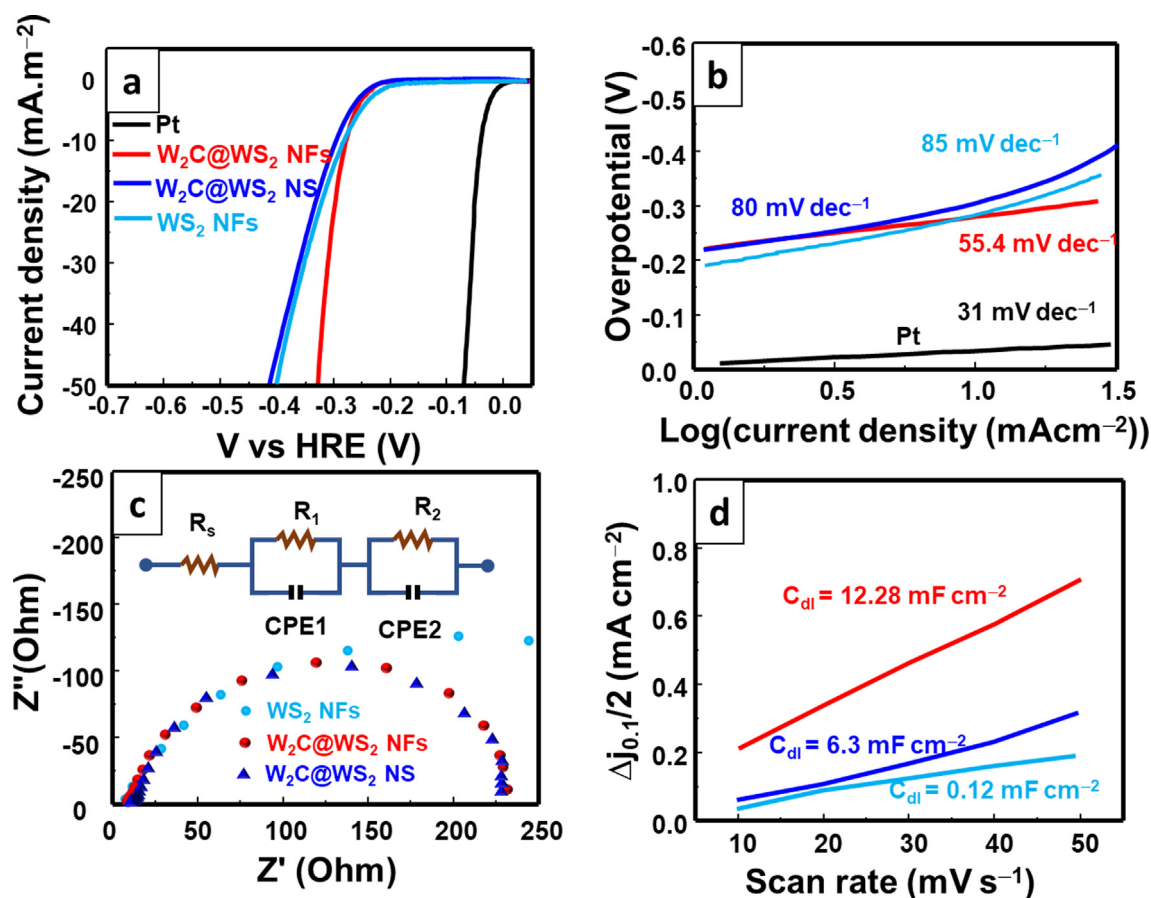


Fig. 6. Hydrogen evolution reaction performance of $W_2C@WS_2$ nanoflowers, nanosheets and WS_2 nanoflower: (a) polarization curves in comparison with standard Pt at a scan rate of 2 mV s^{-1} ; (b) Tafel plots of materials on glassy carbon electrodes; (c) electrochemical impedance spectrum with the inset showing an equivalent circuit and (d) double-layer capacitance of materials.

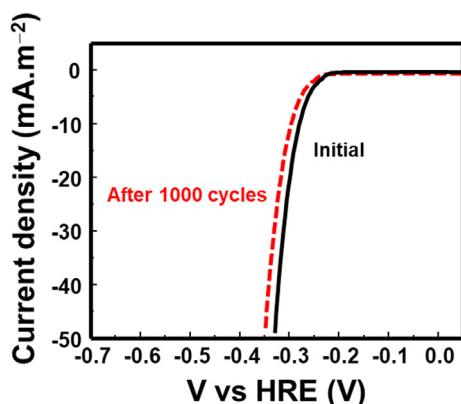


Fig. 7. Stability test of $W_2C@WS_2$ nanoflower after 1000 cycles.

nanoflower (0.12 mF cm^{-2}). This higher value for nanoflowers could be because the nanosheets in the depleted surface has a smaller active area. However, the conductivity of materials was similar for different morphologies, which showed similar charge transfer resistance. The double-layer capacitance of these materials is much higher than that of WS_2 materials and those of some enhanced surface of MoS_2 nanomaterials reported in other studies [27,49]. Finally, the stability test of $W_2C@WS_2$ nanoflower was recorded at the overpotential of 320 mV, as shown in Fig. 7. After 1000 cycles, polarization curve shows a small reduction compared to the initial curve, which indicates the high stability of $W_2C@WS_2$ nanoflower. Therefore, it is thought that the $W_2C@WS_2$ composite alloy could be a potential candidate for water splitting

reaction in large scale system.

4. Conclusion

In this work, we present a facile method to synthesize $W_2C@WS_2$ nanoflower materials with commonly available sources of W and S without using the complex carbon or polymer source. The morphologies, structures, and composition of materials were studied by using XRD, FE-SEM, AFM, Raman spectra, and XPS. The size of $W_2C@WS_2$ flowers was measured to be approximately 200–400 nm. The Tafel slope and the onset potential of $W_2C@WS_2$ are 55.4 mV dec^{-1} and 170 mV, respectively. The materials exhibited a stable charge transfer resistance of 200Ω for both nanosheets and nanoflower forms and a high double-layer capacitance of 12.28 mF cm^{-2} . Therefore, we believe that this material could possess potential for applications in energy conversion and energy storage such as supercapacitors and battery devices.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2019.144389>.

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